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Study of a Mathematical Theory for the
Coagulation Kinetics of Colloidal Solutions

BY M. von Smoluchowski

III. Mathematical Theory of Rapid Coagulation

The theory of coagulation, briefly termed "rapid"
which results in the case of complete discharge ⁽¹⁾ of the
double layer, should become more precisely developed in the
following pages under the assumption that we are dealing with
a colloidal solution which originally consists of spherical
particles which are truly of equal size, whose number per unit of
volume is represented by v_0 . Owing to the electrolytic effect
which can take place in the entire liquid instantaneously and
equilatorally, in a point of time where $t = 0$, every particle has
become provided with a sphere of attraction of radius R . From
now on its Brownian Molecular Movement will go on undisturbed in
its normal way until the point of time when - really because of
that very movement - the center of another particle comes into
its sphere of attraction. From this moment on the pair in
question because of their combining should constitute an indivisible
unit which resumes its Brownian movement of increased velocity

corresponding to the increase in volume. By the combining of further primary particles to the double particles, and by union of two double particles or a single and a triple particle, triple and quadruple particles can arise, and in this manner the coagulation process is carried out until the entire particulate substance has changed into an agglomerated mass providing that a sedimentation of the aggregate had not already occurred due to the force of gravity.

The mathematical problem to be solved resides in the calculation of the numbers v_1, v_2, v_3, \dots of the simple, double, triple... particles which exist at time t , on the basis of the estimate of the sizes which characterize the entire system, namely the original number v_0 , the value of the effective radius R and the velocity constant D of the Brownian motion.

Certain conclusions can be drawn now without special calculation, generally on the basis of the fact that progress of the coagulation should be a function of its three values.

From this scheme of dimensions:

$$v_0 \sim l^{-3}; R \sim l^{-1}; D \sim l^2 t^{-1}$$

one sees namely that the value D is the only one which is connected with the time scale. Since the latter can have no influence on the absolute progress of coagulation, then this must necessarily be a simple function of the product (Dl) . Owing to this -- in the case of given v_0 and R -- the duration of time necessary for attaining a certain stage of the coagulation must be inversely proportional to the diffusion constant D .

One can also estimate by this means the influence of temperature if one assumed, which the experimental results as regards the Quantity R (see the next section) suggests, that the effective radius R is not dependent on the temperature. Then the coagulation time should vary proportionally to the ratio Λ/θ with regard to the formula. (2)

$$(1) \quad D = \frac{H \theta}{N} \frac{1}{3 \pi \eta a} \quad (1)$$

Thus they were in the case of varying temperature indirectly proportional to the viscosity of the medium which agrees with some studies already carried out by Zsigmondy concerning this matter.

Since we now turn to the actual calculation, we should first consider a simplified problem in which we imagine that one of the particles is fixed and that only this one possesses a sphere of attraction, while the rest of the particles do not coagulate with each other.

How large is the probability, under these conditions that, in a time t , a particle has become attached to the particle mentioned above?

This question can be answered most simply on the basis of the equivalence of the Brownian molecular motion and the diffusion mechanism (3). The process which we call diffusion is basically simply the resulting total effect of the Brownian motion of the individual particles. Every one moves independent from the others, according to the diffusion formula:

$$(2) \quad w(x) dx = \frac{1}{\sqrt{4 \pi D t}} e^{-\frac{x^2}{4 D t}} dx \quad (2)$$

This states with what probability a particle leaving from

the zero point would reach in the time t an abscissa $x \dots x \frac{1}{2} dx$, and it can be easily demonstrated mathematically that these movements lead on the average to an equalization of the concentration differences, which is in complete agreement with the above-mentioned diffusion theory.

Thus the coefficient D is found which also occurs in the known equation for the average displacement square as identical with the coefficient of diffusion of the particle swarm:

$$(3) \quad \bar{x}^2 = 2 D t \quad (3)$$

Its value is, in the case of sphere shaped particles, determined by the Einstein formula (1) of which we will make use later.

The provision that the surface of the sphere of radius R retains every particle which joins it, we could obviously compensate by the assumption that they are completely absorbed, that is to say that the concentration zero is continually obtained at the sphere surface R . There arises because of this a concentration gradient in the environs of the sphere, and the substance which diffuses through the surface of the latter in the space of time $t \dots t \frac{1}{2} dt$ corresponds exactly to the average number of particles which hit the sphere because of their Brownian movement in a given time lapse and are adsorbed.

To be sure the equivalence of these two values holds true only as long as this "average number" is very small in relation to the unit, since otherwise the possibility of a simultaneous adsorption of more particles comes into consideration which

must occur otherwise because of the mutual hinderance of the latter. If it is certain that the equivalence is valid, then the number ν_0 is sufficiently small; thus we can accept for the present that we are dealing with the probability of the adsorption of individual particles which exist somewhere inside of the extremely large V.

Now the problem to solve is principally to determine the portion of a substance which generally filled the endless space homogeneously (Starting concentration c), starting from the moment $t = 0$ but diffusing against the surface of the sphere $r = R$, in which from each point of time it is supported at the concentration $u = 0$.

The diffusion equation because of the spherical symmetry assumes the form:

$$(4) \quad \frac{\partial (ru)}{\partial t} = D \frac{\partial^2 (ru)}{\partial r^2} \quad (4)$$

and this equation is fulfilled by the functions

$$(5) \quad (5)$$

$$u = c \left[1 - \frac{R}{r} + \frac{2R}{\sqrt{\pi D t}} \int_0^{\frac{r-R}{\sqrt{4Dt}}} e^{-z^2} dz \right]$$

which at the same time also fulfill our initial and limiting conditions:

1. $u = c$ for $t = 0, r > R$
2. $u = 0$ for $r = R, t > 0$.

Therefore it happens that in the space of time $t \dots t + dt$ the mass diffusing to the sphere R^2 :

$$(6) \quad J dt = 4 \pi D R^2 \frac{\partial u}{\partial r} \Big|_R dt = 4 \pi D R^2 \left[1 + \frac{R}{\sqrt{\pi D t}} \right] dt \quad (6)$$

and the total mass flowing in until the time t :

$$(7) \quad M = \int_0^t J dt = 4 \pi D R^2 \left[t + \frac{2 R \sqrt{t}}{\sqrt{\pi D}} \right] \quad (7)$$

In the sense of what has previously been said, the probability that a certain particle which exists somewhere in space V has fused to the sphere (for $\sigma = \frac{2}{3}$ up until a point of time t amounts to:

$$(8) \quad w_t = \frac{4 \pi D R^2}{V} \left[t + \frac{2 R \sqrt{t}}{\sqrt{\pi D}} \right] \quad (8)$$

The probability that it should not enter in the region R is naturally: $U = 1 - w$ and when all the n -particles were present in the space V , and moved independent of each other, then the probability that no individual of them should be in the region R up to a point of time t is obviously equal to: $(1-w)^n$, which can be replaced for small w and large n by: e^{-nw} .

Since now $\frac{n}{V}$ equals the number of particles per unit volume v , we obtain for the probability that in each time no agglomeration should occur:

(9)

(9)

$$U_s = 1 - 4\pi DR v_0 \left[1 + \frac{2R^2 v_0}{4\pi D} \right]$$

For the purpose of simplifying the calculations, we omit from now on the second term in the brackets, so that we assume that we are studying the course of coagulation at such points of time where the restriction $t \gg \frac{R^2}{D}$ is fulfilled. In the studies of Zsigmondy which will be discussed later, the length of the initial stages thus excluded amounts to approximately 10^3 to 10^4 seconds, which shows that the supplementary terms are practically meaningless.⁽⁵⁾ By doing this all deliberations are highly simplified, since according to ⁽⁶⁾ it can be concluded that probability w of an agglomeration (per unit of time) to the sphere R is constant and is given by the product of $4\pi DR$ and the prevailing number of particles v_0 per unit volume in the spheres surrounding environment (true for $r \rightarrow \infty$):

(10)

$$w = 4\pi DR v_0$$

(10)

If instead of some emphasized particles a number N_0 of the latter now be kept in mind as a condensation nucleus of active particles (which however could not be mutually influenced, thus they must be at relatively large distances from each other), then it would be concluded that for time t the number of simple primary particles which still remained free among them would amount to:

$$(11) \quad N_1 = N_0 e^{-4 \pi D R_0 t} \quad (11)$$

and the number of the agglomerations which occurred in the space of time dt would be:

$$-dN_1 = 4 \pi D R_0 N_1 dt$$

That is, the percent decrease of the number of the simple particles (6) would be given by

$$(12) \quad -\frac{dN_1}{N_1} = 4 \pi D R_0 dt \quad (12)$$

The last is thus the number of particles which collide against the primary particles on the average in the space of time dt , if one assumes that each primary particle is fixed and that in its additional environment the initially given particle number N_1 is maintained.

One could now study therefore in a simple way the determination of the effective velocity variation of the number of primary particles in which one considers the gradual decrease of the latter in the expression on the right side of equation (12), that is in which one replaces N_0 by N_1 . In this manner we obtain the characteristic reaction equation of the second order:

$$(13) \quad \frac{1}{N_1} \frac{dN_1}{dt} = -4 \pi D R$$

which yields the integral:

$$(14) \quad V_1 = \frac{V_0}{1 + 4 \pi D R V_0 \lambda} = \frac{V_0}{1 + \frac{\lambda}{T}}$$

The course in time is thus dependent in a simple way on an individual coefficient:

$$(15) \quad T = \frac{1}{4 \pi D R V_0}$$

which we henceforth will show shortly as "coagulation time"

For this calculation however, two essential corrections are to be entered and especially with regard to:

1. the individual movement which the particles display;
2. the coagulating influence of multiple particles.

Since the extracted particle in immediate consideration is not immovable but its Brownian movements go on in a manner completely analogous to the rest of the particles, one must in transferring the original coordinate points to its mid-point allow the other particles to carry out their effective relative movements.

Now one readily remembers that the relative motion of two particles, whose Brownian movement is independent from each other, act according to the diffusion constants D_1 and D_2 , is again a Brownian molecular movement and indication of such a movement is characterized by a diffusion constant $D_1 + D_2$. Then the probability that the fluctuation from the position of rest attained with the passage of time t amounts to $\xi \dots \xi + \lambda \xi$ resulting as a product of the probabilities which are independent from each other, that one particle has moved to x , the other $\xi + \eta$ which is shown in equation (2) as:

$$w(\xi) d\xi = \int_{-\infty}^{+\infty} w(x) dx w(\xi+x) d\xi = \frac{d\xi}{2\pi \pm \sqrt{D_1 D_2}}$$

$$\int_{-\infty}^{+\infty} x \frac{x^2}{4D_1 \pm} - \frac{(\xi+x)^2}{4D_2 \pm} dx = \frac{\xi^2}{2\sqrt{\pi D_1 + D_2}} d\xi$$

The same formula (2) thus holds true for the relative movement as for the absolute movement but with a coefficient $D_1 = D_2$ and the consideration of the mutual motions must thus be higher than the coefficient D doubled. Therefore the decrease of the number of simple primary particles will be given by the formula:

$$(16) \quad V_1 = \frac{V_0}{1 + 8\pi D R_0 t} = \frac{V_0}{1 + \frac{2x}{t}} \quad (16)$$

By analogy with the equations of the chemical kinetics one can probably expect at the outset an equation of this form, if one, as we have done it up to now, only the uniting of the primary particles with each other has been taken into consideration since such a process corresponds completely to a bimolecular reaction. Now, however, we have yet to consider that a reduction of the primary particles also gives rise to two-, three-, and multiple particles by hitting each other, and indeed

the equation (10) which is analogous to the term in question, will be given by a term of the form $\frac{1}{4\pi} D_{1n} R_{1n} V_n$, in which D_{1n} is an abbreviation for $D_{1n} = D_1 \cdot D_n$ and R_{1n} signifies the radius of the sphere of action, which corresponds to the field of attraction between a simple and an n-multiple particle.

On the whole therefore the decrease of the number of simple particles results in the equation:

$$(17)_1 \quad \frac{1}{4\pi} \frac{dN_1}{dt} = D_{11} R_{11} v_1^2 - D_{12} R_{12} v_1 v_2 - D_{13} R_{13} v_1 v_3 - \dots \quad (17)$$

On the other hand the analogous relationship holds true also for the gradual disappearance of the double particles; however, in this case the positive building velocity is also to be corrected, in which a double particle arises for each two single particles which disappear:

$$(17)_2 \quad \frac{1}{4\pi} \frac{dN_2}{dt} = D_{11} R_{11} v_1^2 - D_{12} R_{12} v_1 v_2 - D_{21} R_{21} v_1^2 - D_{22} R_{22} v_2^2$$

Triple particles are formed by the joining of a single particle with a double one:

$$(17)_3 \quad \frac{1}{4\pi} \frac{dN_3}{dt} = D_{12} R_{12} v_1 v_2 - D_{23} R_{23} v_2 v_3 - D_{31} R_{31} v_1 v_3 - \dots$$

Quadruple particles correspond to the union of 2 double ones, or a single and triple particle:

$$(17)_4 \quad \frac{1}{4\pi} \frac{dN_4}{dt} = \frac{1}{2} D_{22} R_{22} v_2^2 + D_{13} R_{13} v_1 v_3 - D_{34} R_{34} v_1 v_4 - \dots, \text{etc.}$$

An exact furtherance of the calculation is not possible now since D_{ik} and R_{ik} are not exactly calculable for multiple particles, since the latter certainly do not possess spherical shape. Hence one must be content with a certain approximation in which one introduces for the expression in question - with the exception of D_{11} and R_{11} - plausible simplifying assumption. If one limits himself to the initial stage of coagulation as was the case in the measurements of Zsigmondy, then a limited uncertainty which results has little importance, since at the beginning the influence of multiple particles is negligible.

Thus we want to consider also multiple particles as approximating spheres and want to assume that their effective radius is proportional to the radius of the sphere; the latter assumption will ~~not~~ be made obvious by experimental results which will be given later, as a consequence of which R_{11} was given of the order of size of the sphere diameter. Now if two spheres of different radius collide, the natural assumption is - in an analogous manner to the molecular collision in the gas theory -:

$$R_{ik} = \frac{1}{2} (R_i + R_k)$$

If R equals the sphere diameter then it happens that the particles are drawn into contact.

Now since in accordance to (1) the diffusion constants of the particle radius are inversely proportional, it holds true:

$$(12) \quad D_i R_{ik} = \frac{1}{2} (D_i + D_k) (R_i + R_k) = \frac{D_i R_i (R_i + R_k)^2}{R_i R_k} \quad (12)$$

For equal radii it follows that the latter value:

$$D_{ik} R_{ik} = 2 ER,$$

which was assumed at the outset for $D_{11} R_{11}$ and one is convinced that the order of magnitude of the expression under consideration will remain equal in the case of a radii ratio which differs somewhat. Thus for the simplification of the calculations we place the coefficients altogether: (7)

$$(19) \quad 4\pi D_{ik} R_{ik} = 8\pi DR = 2\alpha$$

and thus obtain the equation system:

$$(20) \quad \frac{1}{2\alpha} \frac{dv_1}{dt} = v_1^2 - v_1 v_2 - v_1 v_3 - v_1 v_4 - \dots,$$

$$\frac{1}{2\alpha} \frac{dv_2}{dt} = \frac{v_1^2}{2} - v_1 v_2 - v_2^2 - v_2 v_3 - \dots,$$

$$\frac{1}{2\alpha} \frac{dv_3}{dt} = v_1 v_2 - v_1 v_3 - v_2 v_3 - v_3^2 - \dots,$$

$$\frac{1}{2\alpha} \frac{dv_4}{dt} = \frac{v_2^2}{2} + v_1 v_3 - v_1 v_4 - v_3 v_4 - \dots$$

This allows, in a surprisingly easy manner, complete

integrating in spite of its complicated form. When the

symbol $v_1 \neq v_2 \neq v_3 \neq v_4 \dots \equiv \Sigma v$ is introduced for brevity

as the immediate total number of all particles, then each system assumes the form:

$$(22) \quad \frac{1}{2\alpha} \frac{dv_1}{dt} = -v_1 \Sigma v,$$

$$\frac{1}{2\alpha} \frac{dv_2}{dt} = \frac{v_1^2}{2} v_2 \Sigma v,$$

$$\frac{1}{2\alpha} \frac{dv_3}{dt} = v_1 v_2 - v_3 \Sigma v,$$

$$\frac{1}{2\alpha} \frac{dv_4}{dt} = \frac{1}{2} [v_1 v_{n-1} + v_2 v_{n-2} + v_3 v_{n-3} + \dots + v_{n-1} v_1] - v_4 \Sigma v$$

and by summarizing all the equations one obtains the

$$\text{differential equation for } \Sigma v: \frac{1}{2\alpha} \frac{d\Sigma v}{dt} = -(\Sigma v)^2,$$

from which it follows:

$$(23) \quad \Sigma v = \frac{v_0}{1 + \alpha v_0 t} = \frac{v_0}{1 + 4 \pi D R v_0 t} = \frac{v_0}{1 + \frac{t}{T}}$$

With this expression the remaining equations may now be successively integrated:

(24)

$$v_1 = \frac{v_0}{[1 + \alpha v_0 t]^2} = \frac{v_0}{[1 + 4 \pi D R v_0 t]^2} = \frac{v_0}{[1 + \frac{t}{T}]^2}$$

$$v_2 = v_0 \frac{\alpha v_0 t}{[1 + \alpha v_0 t]^3}$$

$$v_3 = v_0 \frac{[\alpha v_0 t]^2}{[1 + \alpha v_0 t]^4}$$

$$v_4 = v_0 \frac{[\alpha v_0 t]^{k-1}}{[1 + \alpha v_0 t]^{k+1}}$$

(27)

It can be easily noted a posteriori that the general equation (22) is fulfilled by the latter expression so that actually the summary of number of particles gives the expression (25)

Our complete calculation as a result need not assume the number of primary particles but the total number of all particles N_0 according to the simple reaction equation of second degree (23). The number of primary particles decreases very rapidly, so that after the course of the time of coagulation $T = \frac{1}{N_0}$ they amount to only a quarter of the original number.

The number of double particles in contrast increases from zero and indeed increase most rapidly at the outset and attains its maximal value $N_2 = \frac{1}{27} N_0$ in the time $\frac{1}{2} T$, whereupon they again decrease in accelerating amount and finally approaches zero asymptotically. The triplet.. k-multiple particles have initially a very small rate of build up, their number attains successively smaller maximal values:

$$N_k = N_0 \frac{(k-1)^{k-1}}{(k+1)^{k+1}}$$

with the passage of time:

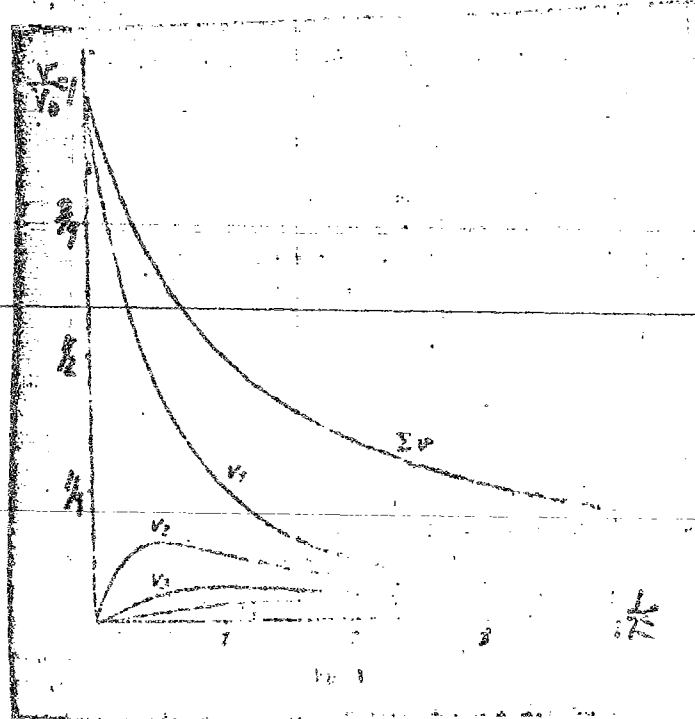
$$t = \frac{k-1}{2} T.$$

The graphical representation (Fig. 1) of the relative number of particles $\frac{N}{N_0}, \frac{N_1}{N_0}, \frac{N_2}{N_0}, \frac{N_3}{N_0}$ is dependent on the time $\frac{t}{T}$ gives a truly clear picture of the entire process of coagulation which was theoretically foreseen.

Thus, if the time in scale of coagulation T is taken as the unit, then the coagulation curves which are presented in relative values of particle numbers are independent of kind and size of the particles, of the concentration of the solution,

of the kind of media, of the temperature etc., it is naturally foreseen that we are dealing with spherical shaped particles. In practical consideration the condition is hereby worthy of note that the coagulation time T , of a given solution could be arbitrarily lengthened by dilution of the solution, even though we are dealing with a "rapid" coagulation, since T must be directly proportional with V_0 and furthermore that T is also in high degree dependant on the kind of particles and kind of medium.

FIG. 1 GRAPHIC NOT REPRODUCIBLE



Footnotes

- (1) Experimentally this extreme case is characterized by the particular features which are explained in section 4.
- (2) As an exception the absolute temperature could be denoted with Θ in this study in order to avoid ambiguity with the coagulation time.
- (3) Concerning these particular items see the address in Göttingen mentioned at the beginning.
- (4) This formula makes possible a treatment of many other analogous cases; it holds true for example for the mass of water vapor, water drops are cooled to a point under the saturation point.
- (5) The neglecting of the supplementary terms is obviously stated also for cases where the number V_0 is variable per unit time, provided only that the variation of V_0 occurs sufficiently slowly, that is provided it is slight inside the lapse of time $\frac{R^2}{D}$. In the following the tacit custom is thus made; it is required that the reciprocal time of coagulation $\frac{1}{\tau} = 4\pi DRV_0$ should be very small in relation to $\frac{D}{R^2}$, and accordingly that $\pi R^2 V_0 \ll 1$ a condition which should be at best invalid for concentrated solutions.
- (6) Here the previously referred to difficulty is done away with, which concerned the multiple association. It was actually in agreement with what was earlier expressed - not exactly

correct to place the probability W for joining to a particle merely as generally equal $4\pi R V_0$ (Equation 10) since the equivalence of the processes of deposition and of diffusion is distorted in case of multiple association. However, there exists complete equivalence for each condensation nucleus V_1 which has as yet undergone no deposition or until a given moment and which gives directly each probability which interests us when we are dealing with the reduction of the number of primary particles. With other expressions: the formula (10) is sufficiently correct when one relates the occurrences of a primary association to the emphasized particles.

(7) Strengt would take, to be sure, the opposite clumping velocity of unequal particles as larger than with equally large particles, which perhaps could be considered if one had made it at the outset with a mixture of particles of very significantly different sizes. With regard to the modifications in cases where the relation (19) is not valid, see the remark on p. 153.